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CERAMIC FOAM MATERIALS BASED ON WASTES FROM PETROCHEMICAL FIELDS

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The use of leucoxene concentrate — a waste from the Yaregskoe Petrochemical Field — as a carbide-forming additive for obtaining ceramic foam materials is examined. Comparative physical – mechanical, thermophysical, and electrical characteristics of the ceramic foam materials obtained are presented and new carbide-forming formulas are proposed.

The development and adoption of highly effective materials that work reliably under extreme conditions is very topical. Under the action of high temperatures and chemically corrosive media, the well-known metallic and ceramic materials in many cases cannot provide the required longevity of structures.

Ceramic foam and carbide foam materials based on polymers which foam up because of their specific chemical and physical properties have found extensive applications in the last few years. These materials retain all high characteristics of carbides but their density is low because of their porous structure.

The carbothermal method was used to obtain ceramic foam and carbide foam materials. Carbon microspheres (CM) were introduced into the initial mixture to ensure porosity. The liquid carbonizing binder (phenolformaldehyde resin — PFR) was the main supplier of the carbon reducing agent. Finely dispersed powders of titanium and silicon as well as their oxides were used as the carbide-forming additives.

However, even though ceramic foam materials have good thermophysical and physical – mechanical properties, they are not extensively used because of the high cost of the carbon microspheres, which are obtained by carbonization of phenol microspheres (PM) at 800°C, and the powders of the metals as well as their oxides.

The objective of the present investigation is to find a suitable substitute for carbide-forming materials and pore-forming material without degrading the physical – mechanical and thermophysical properties of the ceramic foam materials.

Leucoxene concentrate (LC) — a waste from the Yaregskoe Petrochemical Works — can serve as a good carbide-forming additive for the production of ceramic foam materials, since it is mainly a mixture of silicon and titanium oxides (30%[2] SiO_2, 60% TiO_2), capable of forming carbides. Hollow ceramic microspheres (HCM) can be used as the pore formers. Abroad, these materials are called cenospheres. HCM comprise part of the smoke emissions of coal-burning heat plants. The main components of HCM are SiO_2 (60%) and Al_2O_3 (28%).

The physical – mechanical properties of ceramic foam materials are presented in Table 1. Analysis of the measurements of the apparent density, compression strength, thermal conductivity, and resistivity of the samples shows the following.

As the amount of leucoxene decreases and the mass of the microspheres increases in the initial mixture, the apparent density of the foam materials decreases in all cases, irrespective of the type of microspheres. When the amount of leucoxene introduced exceeds 50%, the density becomes a linear function of the microsphere content (MS).

The density of a material with HCM is much higher — $(1.1 - 1.6) \times 10^3$ kg/m^3 — than the density with carbon microspheres. This is due to the smaller diameter of the ceramic microspheres than that of the carbon microspheres. Apparently, this difference should affect other properties of the materials.

The dependences of the compression strength on the concentration of the components in the initial mixture are not single-valued and are less pronounced, in contrast to the density. The strength of the material with HCM (17 – 21 MPa)

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[2] Here and below: mass content.

TABLE 1.

Initial mixture composition, %			Properties of foam materials			
additive	MS	PFR	density, 10^{-3} kg/m^3	compression strength, MPa	electric conductivity, S/m	thermal conductivity, W/(m · K)
SiO_2:	CM:					
55	20	25	0.30	0.4	10	0.35
78	5.5	16.5	0.65	6.5	40	0.50
TiO_2:	CM:					
55	20	25	0.60	0.7	500	0.70
83	4	13	1.50	8.0	135	0.90
Si:	CM:					
58	9	33	0.70	5.6	40	0.60
64	13	23	0.77	7.5	25	0.75
Ti:	CM:					
75	9	16	1.35	7.0	10,000	0.60
80	6	14	1.65	15.0	16,000	0.85
LC:	PM:					
50	22	28	0.60	3.9	915	0.40
64	15	21	0.72	2.6	450	0.60
64	12	24	0.89	2.7	810	0.70
80	5	15	1.24	1.0	100	1.25
LC:	CM:					
50	23	27	0.64	2.3	1060	0.45
64	16	20	0.76	2.5	700	0.65
64	13	23	0.94	2.8	880	0.75
80	5	15	1.35	4.2	80	0.95
LC:	HCM:					
50	31	19	1.08	12.6	160	0.75
60	25	15	1.17	14.1	150	0.95
60	21	19	1.25	17.6	155	1.05
75	10	15	1.52	20.0	140	1.25

increases sharply, and the samples are also stronger than those containing phenolformaldehyde and carbon microspheres.

In most cases, the thermal conductivity depends on the composition and porosity of the material. The heat-insulating properties can be improved by increasing the porosity, but in a number of cases the porosity of the articles must be decreased in order to increase their stability. Depending on their specific use conditions the materials can possess high density and low porosity (with titanium powder added as carbide-forming agent) and, conversely, a highly porous low-density structure (with silicon oxide powder as the additive).

As the density increases, the thermal conductivity of the material increases. In addition, the thermal conductivity of the material with HCM is higher than that of the samples with carbon microspheres.

The electric conductivity of synthesized foam materials is determined by the number and mobility of the current carriers (ions and electrons) in the components of the initial mixture and in the products of carbonization and carbidization, and it also depends on the structure and porosity of the material. In the solid state, the initial components — silicon, titanium, aluminum, and iron oxides, phenolformaldehyde resin and carbon — have practically zero electric conductivity (carbon is an exception).

TABLE 2.

Initial mixture composition, %				Properties of foam materials		
LC	MS	PFR	powder of element	density, 10^{-3} kg/m^3	compression strength, MPa	electric conductivity, S/m
	PM:		Ti:			
71	8	17	4	1.32	6.23	490
73	6	15	6	1.52	10.67	370
73	4	13	10	1.65	8.16	290
	CM:					
73	8	14	5	1.40	13.02	235
74	6	12	8	1.48	7.76	415
73	4	12	11	1.62	13.85	545
	PM:		Si:			
71	8	18	3	1.23	7.34	205
73	6	16	5	1.39	8.64	175
73	4	14	9	1.47	8.29	105
	CM:					
72	8	16	4	1.34	10.80	510
73	5	16	7	1.57	16.62	380
73	4	12	11	1.44	6.37	120

After a material undergoes carbidization (1100 – 1500°C) the electric conductivity should increase, since the oxides are converted in carbides, of which titanium carbide possesses metallic conductivity (plus residual carbon).

The measurements show that the electric conductivity of the samples as a whole decreases as the leucoxene concentration increases.

If the foam materials with phenol and carbon microspheres differ only negligible with respect to the conductivity, the samples with HCM pass electric current appreciably worse. This is due to the composition of HCM (about 70% SiO_2). Silicon carbides are formed under heat treatment, and because covalent bonds predominate in them their electric conductivity is low.

The properties of foam materials with added silicon and titanium powders after carbidizing heat treatment are presented in Table 2. Compared with the corresponding properties of the materials without silicon and titanium additives, the density and electric conductivity of the samples obtained increase only negligibly. The density and conductivity of the samples with titanium additive are higher than that of the material with silicon.

The compression strength of all samples with silicon and titanium powder added is higher than for similar samples without the additives (6 – 16 MPa). This shows that it is desirable to introduce 5 – 7% powders of the elements in order to increase the mechanical strength. There is virtually no difference in strength with the addition of silicon or titanium. For materials with carbon microspheres, the electric conductivity is higher than in samples with phenolformaldehyde microspheres.

In summary, it is now possible to produce comparatively inexpensive but quite effective ceramic foam materials based on synthetic plastic foams using hollow ceramic microspheres and wastes from a petrochemical field. The ecological problems associated with the utilization of stack emission and wastes from petrochemical fields are solved in the process.

The corrosion and heat resistance, the thermal conductivity and density which can be regulated over wide limits with quite high mechanical strength, and the comparatively low cost of the foam materials produced are a hopeful prerequisite for their use in different fields of technology and industry.

Their easy mechanical workability makes it possible to fabricate from them articles with virtually any shape and size, and this makes it possible to use them as structural materials.